Measurements of the fates of substituted alkoxy radicals

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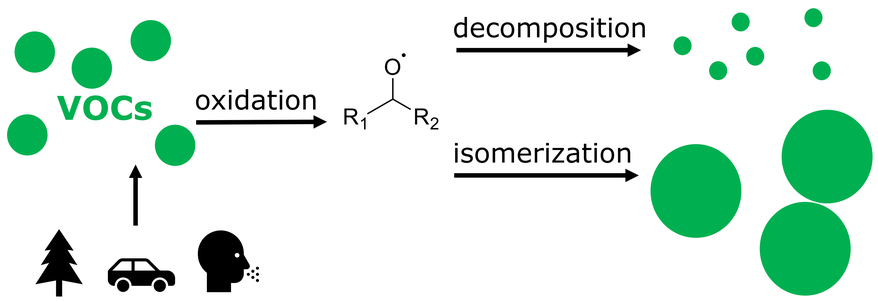
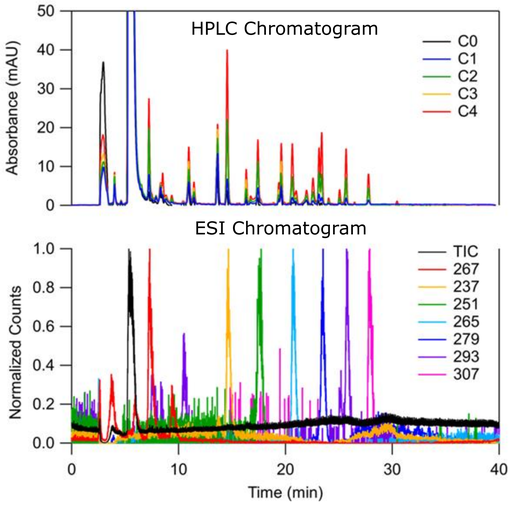
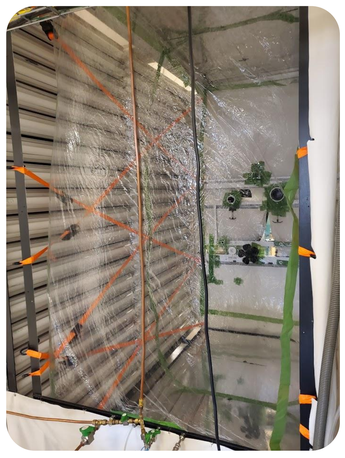


Motivation

- Volatile organic compounds (VOCs) are emitted from natural sources, human activities, and humans themselves
- Atmospheric oxidation often leads to alkoxy radical intermediates
- Alkoxy radical isomerization leads to larger products, forming more aerosol
- Decomposition leads to smaller products, less likely to form aerosol
- Branching between decomposition and isomerization still poorly understood





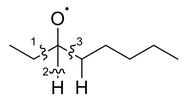
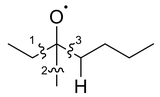
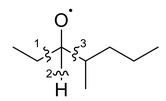
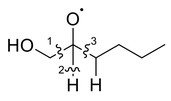
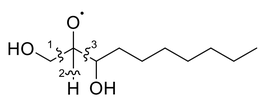
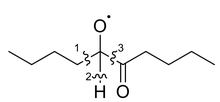
Methodology

- Experiments performed in an 8 m^3 Teflon chamber
- Generate specific alkoxy radicals via photolysis of synthesized alkyl nitrites
- Quantify gas-phase carbonyl products with offline methods
  - DNPH cartridges → HPLC-ESI-ToF-MS
  - PFBHA coated denuders → HPLC-ESI-ToF-MS
  - Tenax → GC-FID
- Method sampling efficiencies confirmed with offline calibrations and additions of standards to chamber.

Results

- Measured carbonyl concentrations consistent between methods
- Isomerization branching determined by difference
- Compare with predictions made by structure-activity relationships (SARs)
- Decent agreement for simple alkyl alkoxy radicals
- Both SARs strongly overpredict decomposition for hydroxyl and carbonyl alkoxy radicals
- Further work will investigate branching of nitrates and multifunctional compounds

Measured and predicted alkoxy radical branching ratios.

Alkoxy Radical Structure	Reaction	Measured[a]	Predicted (SAR 1[b])	Predicted (SAR 2[c])
	1	*n.d.*[d]	0.6%	0.3%
	2 (+ O_2)	4.0%	1.2%	1.2%
	3	*n.d.*	0.6%	0.5%
	Isomerization[e]	96.0%	97.6%	98.0%
	1	1.6%	18.7%	1.5%
	2	0.1%	0.1%	0.0%
	3	2.0%	18.7%	2.8%
	Isomerization[e]	96.2%	62.5%	95.6%
	1	0.7%	0.2%	0.2%
	2 (+ O_2)	0.9%	0.4%	1.1%
	3	12.5%	65.3%	7.4%
	Isomerization[e]	85.9%	34.1%	91.3%
	1	18.3%	86.0%	84.8%
	2 (+ O_2)	0.8%	0.2%	0.2%
	3	*n.d.*	0.1%	0.0%
	Isomerization[e]	80.9%	13.7%	15.0%
	1	52.7%	0.3%	4.1%
	2 (+ O_2)	*n.d.*	0.0%	0.1%
	3	9.8%	99.6%	90.8%
	Isomerization[e]	37.6%	0.1%	5.1%
	1	0.9%	0.0%	0.0%
	2 (+ O_2)	1.5%	0.0%	0.0%
	3	41.1%	100.0%	100.0%
	Isomerization[e]	56.5%	0.0%	0.0%

[a] Measured values are averages of applicable measurements

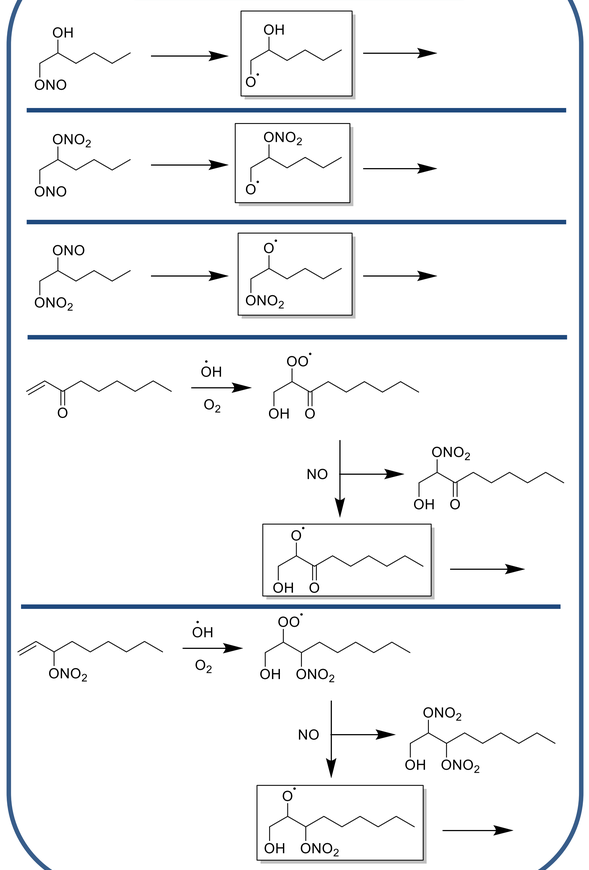
[b] Novelli et al, 2021

[c] Atkinson, 2007

[d] Not detected

[e] Calculated by difference

Systems yet to be studied



Conclusions

- Simple alkoxy radical branching ratios predicted by SARs
- More complex radicals less likely to decompose than expected
- Increased isomerization leads to more functionalization and more SOA

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